Chapter I

INTRODUCTION

AND

LITERATURE STATUS
CONTENTS

CHAPTER I: INTRODUCTION AND LITERATURE STATUS

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1.1. Introduction to TiO$_2$

Titanium dioxide discovered in 1821, is considered to be one of the top 20 inorganic chemicals of industrial importance [1]. Ever since its commercial production began around 1916, an exponential growth of research has been seen in this area [2-4]. Titanium dioxide does not occur in nature but is derived from ilmenite or leucoxene ores. It was identified in black sand from Menacchan Valley in Cornwall. German chemist M. H. Klaproth discovered the element in the TiO$_2$ form, as rutile [5]. Since it falls in group 4 of the periodic table, it shows the characteristic valence of 4 (TiO$_2$), but in addition to that di (TiO) and trivalent (Ti$_2$O$_3$) valence states are reported in some compounds.

Titanium dioxide also known as titania is the most widely used white pigment [6] because of its brightness and a high refractive index. In 1972, Fujishima and Honda [7-9] discovered the photocatalytic splitting of water on TiO$_2$ electrodes and since then it is highly investigated as a photocatalytic and photoelectrochemical material. It is also the most preferred semiconductor photocatalytic material due to its favourable properties like non toxicity, chemical inertness, stability over a wide pH range under irradiation condition [10] and its relatively favourable disposition of band edges [11]. Microcrystalline TiO$_2$ powders are also widely employed in the field of heterogeneous catalysis as active component as well as catalyst support.

In recent times, the use of titania has been extended to medical applications such as use in an artificial heart valve and in dental implants [12,13].

A growing interest in the development of well structured, porous, high surface area and complex forms of titania based materials has led to uses of titania in these various
novel applications [4,14]. These applications depend not only upon the properties of TiO\textsubscript{2} itself but also on the crystalline modifications of TiO\textsubscript{2}.

Some well known characteristics of TiO\textsubscript{2} are:

- it is amphoteric in nature
- it is insoluble in water as well as acids
- it shows high room temperature resistivity, with specific resistivity of 9500 $\Omega$·m
- it has a melting point of 1610 °C and boiling point of 3000 °C
- it shows temperature dependent paramagnetic susceptibility

Figure 1.1 shows the applications of TiO\textsubscript{2} in various fields.

![Diagram of TiO\textsubscript{2} applications](image)

**Figure 1.1:** Various applications of TiO\textsubscript{2}

1.2. Crystalline modifications of titania
Titania exists in the crystalline as well as amorphous forms. The three most studied crystalline modifications of titania are Anatase, Rutile and Brookite. Each crystalline structure exhibits specific physical properties such as band gap, surface states, etc. [15,16] governing their applications and uses.

Anatase and rutile are well known photocatalysts with anatase generally showing much higher photocatalytic activity [17-21]. Rutile is commonly used as a white pigment in paints [22] and brookite is not yet of commercial interest but a dye sensitized solar cell (DSSC) has been reported [23]. Anatase and rutile are both tetragonal in structure while the brookite structure is orthorhombic. In case of all the crystalline forms, each Ti$^{4+}$ ions are surrounded by an irregular octahedron of oxide ions. In the rutile structure each octahedron is in contact with 10 neighbour octahedrons (two sharing edge oxygen pairs and eight sharing corner oxygen atoms) while in anatase structure each octahedron is in contact with eight neighbours (4 sharing an edge and four sharing a corner). The octahedral linkage in brookite is such that three edges are shared per octahedron [24].

Figure 1.2 shows the crystal structures of anatase, rutile and brookite titania.
Figure 1.2: Crystal structure of (A) Anatase titania (B) Rutile titania and (C) Brookite titania [25]
The structure of rutile and anatase can be described in terms of chains of \([\text{TiO}_6]\) octahedra, where each \(\text{Ti}^{4+}\) ion is surrounded by an octahedron of six \(\text{O}^{2-}\) ions.

The two crystal structures i.e. anatase and rutile often differ in distortion of each octahedron and by the assembly pattern of the octahedra chains.

Figure 1.2a shows the unit cell structures of rutile and anatase crystals.

![Structure of rutile and anatase TiO\(_2\) [26-28]](image)

The octahedron in rutile is not regular, showing a slight orthorhombic distortion while the octahedron in anatase is significantly distorted so that its symmetry is lower than orthorhombic. The Ti-Ti distances in anatase are greater (3.79 and 3.04 Å vs 3.57 and 2.96 Å in rutile) whereas Ti-O distances are shorter than in rutile [27] (1.934 and 1.980 Å in anatase vs 1.949 and 1.980 Å in rutile). A comparative study of different crystalline modifications of Titania [25,29] is summarized in Table 1.1.
**Table 1.1: Comparative study of different phases of titania**

<table>
<thead>
<tr>
<th></th>
<th>Rutile</th>
<th>Anatase</th>
<th>Brookite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula Weight</td>
<td>79.890</td>
<td>79.890</td>
<td>79.890</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Point Group</td>
<td>4/m 2/m 2/m</td>
<td>4/m 2/m 2/m</td>
<td>2/m 2/m 2/m</td>
</tr>
<tr>
<td>Space Group</td>
<td>P4_2/mnm</td>
<td>I4_1/amd</td>
<td>Pbca</td>
</tr>
<tr>
<td>Unit Cell</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a(Å)</td>
<td>4.5845</td>
<td>3.7842</td>
<td>9.184</td>
</tr>
<tr>
<td>b(Å)</td>
<td>-</td>
<td>-</td>
<td>5.447</td>
</tr>
<tr>
<td>c(Å)</td>
<td>2.9533</td>
<td>9.5146</td>
<td>5.145</td>
</tr>
<tr>
<td>Volume of the elementary cell (nm³)</td>
<td>62.07</td>
<td>136.25</td>
<td>257.38</td>
</tr>
<tr>
<td>Molar Vol (cm³/mol)</td>
<td>18.693</td>
<td>20.156</td>
<td>19.377</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>4.2743</td>
<td>3.895</td>
<td>4.123</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1830-1850</td>
<td>Transformation to rutile</td>
<td>Transformation to rutile</td>
</tr>
<tr>
<td>Major Applications</td>
<td>White paint</td>
<td>Photocatalyst</td>
<td>DSSC</td>
</tr>
</tbody>
</table>
1.3. Phase transformation: Anatase to Rutile

Generally, titania is obtained either from minerals or from a solution of titanium salts or alkoxides. Most of the literature states, that alkoxide-based sol-gel or precipitation process yield amorphous titania pre-cursors [30]. It is also known that the transformation behaviour from amorphous to anatase or rutile phase is influenced by the synthesis conditions. Besides, the various factors affecting the phase transformation are temperature, pressure, particle size, additives/dopants, impurities and hydrothermal conditions.

Some of the factors affecting the phase transition are discussed below:

(i) Temperature: The heat treatment of amorphous titania converts it to a crystalline anatase structure at temperature below 400 °C, which is further converted to rutile form when heated between 600 °C- 1100 °C [31,32].

The anatase to rutile phase transformation is envisaged as a transformation from a metastable state to stable state. However no unique phase transformation temperature is reported [33]. Li et al. [34] found that the anatase to rutile phase transformation occurred in the temperature range of 700-800 °C. Both anatase and rutile particle sizes increased with the increase of temperature, but the growth rate was different. Rutile had a much higher growth rate than anatase. The growth rate of anatase leveled off at 800 °C. An increased lattice compression of anatase with increasing temperature was observed.
N. Jagtap et al [35] studied the onset of transformation temperature by subjecting anatase titania to heat treatment from 423 K (150 °C) to 1173 K (950 °C).

Figure 1.3 shows the expected anatase to rutile phase transformation as the temperature is increased from room temperature to 1173 K (950 °C).

Figure 1.3: The multiple plots of powder XRD patterns of the titania sample scanned in air at various temperatures [35]

As seen from Figure (1.3), the onset of transformation temperature for anatase in air was 1023 K (750 °C) and complete transformation for anatase to rutile occurred at 1173 K (900 °C).
It was also found that the anatase sample showed higher stability in vacuum as compared to air atmosphere. The transformation of anatase to rutile is suppressed due to lack of oxygen and only 3\% of anatase is transformed to rutile at 900 °C. The unit cell parameters ‘a’ and ‘c’, and the unit cell volume increase linearly with increase in temperature under both the atmospheres (air and vacuum).

Though rutile is the more stable phase at high temperatures, Zhang et al [36,37] showed that anatase and brookite are common in fine grained (nanoscale) natural and synthetic samples. On heating concomitant with coarsening, the following transformations are all seen

- anatase to brookite to rutile,
- brookite to anatase to rutile,
- anatase to rutile and brookite to rutile

Ye et al. [38] concluded that brookite could not transform directly to rutile but had to transform to anatase first. However, direct transformation of brookite to rutile was observed above 700 °C by Kominami et al [39].
(ii) Additives/Dopants: Talavera and co-workers [40] demonstrated that anatase to rutile phase transformation depends strongly on the kind of cation (Li$^+$, K$^+$, Zn$^{2+}$, Al$^{3+}$) used to dope the titania material. When different metal ions are used, phase transition occurs at different temperatures. Presence of additives such as alumina, silica, zirconia, sulphate ions etc. in TiO$_2$ can stabilise the anatase phase [41-43] whereas presence of chloride ions has an accelerating effect on the anatase to rutile phase transformation under hydrothermal conditions [44,45].

The mechanism by which the additives either inhibit or promote the anatase to rutile phase transformation is related to the defect structure of titania i.e, the concentration of oxygen vacancies or Ti interstitials. Essentially the dopants create an oxygen deficiency in the crystal structure of titania [46].

The cations and the anions in titania are both reported to need some room to move to commence the phase transition. The structure becomes contracted at the end of this process producing the rutile phase [47].

In this regard the oxygen deficiency is reported to facilitate the anatase-rutile phase transition. However some additives retard the transformation by increasing the lattice defects of Ti interstitials in titania [48].
(iii) **Hydrothermal conditions:** Swamy et al [49] found that the metastability of anatase as a function of pressure was size dependent, with smaller crystallites preserving the structure to high pressures. Barnard et al [5-54] found that surface passivation had an important impact on nanocrystal morphology and phase stability. The results showed that surface hydrogenation induced significant changes in the shape of rutile nanocrystals, but not in anatase, and that the size at which phase transition might be expected increases dramatically when the undercoordinated surface titanium atoms were H-terminated.

The crystal structure of TiO$_2$ nanoparticles depended largely on the preparation method [55]. For small TiO$_2$ nanoparticles (<50 nm), anatase seemed more stable and transformed to rutile at >700 °C. Banfield et al. [36,56] found that the prepared TiO$_2$ nanoparticles had anatase and/or brookite structures, which transformed to rutile after reaching a certain particle size. Once rutile was formed, it grew much faster than anatase. In a later study, Zhang and Banfield [37] found that the transformation sequence and thermodynamic phase stability depended on the initial particle sizes of anatase and brookite. They concluded that, for equally sized nanoparticles, anatase was thermodynamically stable for sizes < 11 nm, brookite was stable for sizes between 11 and 35 nm, and rutile was stable for sizes > 35 nm. Larger distortions existed in samples with smaller particle size.
1.4. Synthesis of TiO₂

In industry, TiO₂ pigments are produced by older sulphate process or newer chloride process as shown in Figure 1.4 and Figure 1.5 respectively.

The sulphate process: The sulfate process was the first commercial scale technology used to convert ilmenite to TiO₂. The starting materials for TiO₂ production in this process are ilmenite and titaniferous slag. The process starts with digestion of finely ground raw materials in an exothermic reaction with sulfuric acid. The sulphate process gets its name from the fact that, in this process the titanium raw material is dissolved in sulfuric acid. Titanium oxysulphate thus formed is then hydrolyzed to titanium oxyhydrate by heating the clear solution with steam at 95-110 °C. The hydrolysis product is washed free of impurities and surface treated. TiO₂ obtained in this way usually has the structure of anatase since the sulphate ions stabilize this modification [57].
Figure 1.4: TiO₂ pigment manufactured by the sulphate process [58]
The chloride process: In this process, the starting materials used for TiO$_2$ production are leucoxene, rutile and synthetic rutile. Titanium raw material is chlorinated to form titanium tetrachloride. Following purification steps, the tetrachloride is oxidized in the gaseous phase to titanium dioxide which is subsequently surface treated as in the sulphate process. TiO$_2$ obtained in this way has the mixed structure of anatase and rutile with average diameter of about 20 nm. The newer chloride process offers tighter product control, less labour intensive, avoids the iron sulfate waste problem at larger scales and is cheaper to operate. Sulphate process was the first commercial scale technology used to convert ilmenite to rutile, however the chloride process eventually became a preferred process.
Figure 1.5: TiO$_2$ pigment manufactured by the chloride process [59]
On a laboratory scale, titanium dioxide has been prepared mainly by use of titanium isopropoxide or alkoxides as precursor. Titanium alkoxides can be converted to TiO$_2$ powder by various methods such as sol-gel method, hydrothermal method, chemical vapor deposition, microwave method, micelle and inverse micelle method, solvothermal method and so on. Some of the synthesis methods adopted for the preparation of TiO$_2$ by using titanium alkoxide precursor are discussed in detail:

(i) **Sol-gel method:** In a typical sol-gel process, a colloidal suspension or a sol is formed from the hydrolysis and polymerization reactions of the precursors (metal alkoxides). Complete polymerization and loss of solvent leads to the transition from the liquid sol into a solid gel phase. Further treatment of the gel can produce dense thin films, ceramic fibers, ceramic powders and aerogel (as shown in Figure 1.6). Under proper synthesis conditions nanomaterials can be obtained.
In a typical synthesis, titanium alkoxide is added to the base at 2 °C in alcoholic solvents in a three necked flask and is heated between 50-100 °C for specific time. A secondary treatment involving autoclave heating is carried out to improve the crystallinity [61]. A series of thorough studies have been conducted by Sugimoto et al. using sol-gel method on formation of TiO$_2$ nanoparticles of different sizes and shapes by tuning reaction parameters [62-66]. Recently nanosized TiO$_2$ has been synthesized from titanium tetraisopropoxide via sol-gel method using acid as a catalyst and the optimized conditions concerning the proportional amount of acid, water and alcohol is established [67].
(ii) **Hydrothermal method:** Hydrothermal synthesis is normally conducted in steel pressure vessels called autoclaves with or without Teflon liners under controlled temperature and/or pressure with the reaction in aqueous solutions (Figure 1.7). The temperature can be elevated above the boiling point of water, reaching the pressure of vapour saturation. This method is widely used for the production of small particles in the ceramics industry.

![Figure 1.7: A typical autoclave used in hydrothermal synthesis [68]](image)

TiO$_2$ nanoparticles are normally synthesized by this method by adding titanium alkoxide to distilled water by adjusting the desired pH with HNO$_3$ or NH$_4$OH. The mixed solution is then poured into the hydrothermal vessel and treated at 80-100 °C for few hours [69-71].
(iii) Solvothermal method: The solvothermal method is almost identical to the hydrothermal method except that the solvent used here is non-aqueous. However, the temperature can be elevated much higher than that in hydrothermal method, since the variety of organic solvents with high boiling points can be chosen. The solvothermal method normally has better control than the hydrothermal methods with respect to size, shape and crystallinity of TiO$_2$ nanoparticles.

The solvothermal method has mainly been employed to synthesize TiO$_2$ nanoparticles and nanorods, with/without the aid of surfactants. In a typical procedure by Kim and co-workers [72], titanium tetraisopropoxide was mixed with toluene at different weight ratios and kept in an autoclave at 250°C for 3 h. The average particle size of the TiO$_2$ powders tended to increase as the composition of titanium isopropoxide in the solution increased. TiO$_2$ nanorods in pure anatase crystal phase have also been synthesized by solvothermal method using Ti (IV)-isopropoxide and benzyl alcohol with the addition of acetic acid to the reaction mixture [73].
(iv) **Chemical vapor deposition:** Chemical vapor deposition (CVD) refers to any process in which materials in a vapor state are condensed to form a solid-phase material. These processes are normally used to form coatings to alter the mechanical, electrical, thermal, optical, corrosion resistance and wear resistance properties of various substrates. Recently they have been widely explored to fabricate various nanomaterials. Vapor deposition processes usually take place within a vacuum chamber. If no chemical reaction occurs, this process is called physical vapor deposition (PVD). In CVD processes thermal energy heats the gases in the coating chamber and drives the deposition reaction (Figure 1.8).

**Figure 1.8:** Schematic diagram of low pressure CVD [74]
Thick crystalline TiO$_2$ films with grain sizes below 30 nm as well as TiO$_2$ nanoparticles with sizes below 10 nm can be prepared by pyrolysis of titanium tetraisopropoxide in a mixed helium/oxygen atmosphere, using liquid precursor delivery [75]. When deposited on the cold areas of the reactor at temperatures below 90 °C with plasma enhanced CVD, amorphous TiO$_2$ nanoparticles can be obtained and crystallize with a relatively high surface area after being annealed at high temperatures [76]. TiO$_2$ nanorod arrays with a diameter of about 50-100 nm and a length of 0.5-2 µm can be synthesized by metal organic CVD (MOCVD) on a WC-Co substrate using TTIP as the precursor [77].

Among all these procedures, sol-gel method has received attention for the past decade due to less energetic conditions, possibility of preparing powders or thin films with controlled properties, purity and homogeneity [78]. Chemistry of precursor is known to influence the hydrolysis process. There are several other factors like temperature, pH, type of solvent, route of synthesis, presence of certain ions that are known to influence the phase composition [79]. Each application of titania requires a specific structure and also a specific size, hence it is important to develop synthesis methods in which the size and structure of TiO$_2$ can be controlled [80,81].

Besides titanium alkoxide, the various precursors used for synthesis of TiO$_2$ are titanium tetrachloride, titanium trichloride, titanous sulphate, titanium butoxide, tetrabutyl orthotitanate etc. A brief literature status of TiO$_2$ synthesis using titanium alkoxide, TiCl$_3$ and TiCl$_4$ is given in Table 1.2, 1.3 and 1.4 respectively.
Table 1.2: A brief literature status of TiO$_2$ synthesis using titanium alkoxide as precursor

<table>
<thead>
<tr>
<th>Method of synthesis</th>
<th>General</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sol-gel method by mixing triethanolamine and titanium isopropoxide (TIP)</td>
<td>TiO$_2$ nanoparticles</td>
<td>66</td>
</tr>
<tr>
<td>Sol-gel hydrolysis and precipitation of titanium isopropoxide in ethanol followed by calcinations or hydrothermal treatment</td>
<td>Anatase and Rutile nanocrystals</td>
<td>82</td>
</tr>
<tr>
<td>Hydrolysis of titanium tetraisopropoxide (TTIP) in dry propanol with nitric acid and acetic acid</td>
<td>TiO$_2$ colloids</td>
<td>83</td>
</tr>
<tr>
<td>Hydrolysis of TTIP under glacial acetic acid in presence of water</td>
<td>Anatase TiO$_2$</td>
<td>84</td>
</tr>
<tr>
<td>Hydrolysis and condensation of TTIP in ethanol using nitric acid as an acid catalyst</td>
<td>TiO$_2$ membranes</td>
<td>85</td>
</tr>
<tr>
<td>Modified sol–gel route from TIP modified with acetic acid in order to control hydrolysis and condensation reactions</td>
<td>Anatase TiO$_2$</td>
<td>86</td>
</tr>
<tr>
<td>Hydrolysis of TTIP in solvent/water in presence of soluble starch</td>
<td>Mesoporous TiO$_2$</td>
<td>87</td>
</tr>
<tr>
<td>Ti (IV) n-butoxide ethanol solution was prehydrolyzed in presence of nitric acid, added to deionised water followed by aging</td>
<td>Mesoporous TiO$_2$</td>
<td>88</td>
</tr>
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Table 1.3: A brief literature status of TiO$_2$ synthesis using titanium trichloride as precursor

<table>
<thead>
<tr>
<th>Method of synthesis</th>
<th>General</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct oxidation of TiCl$_3$(aq) stirred for 60 h at RT or for 48 h at 80°C</td>
<td>Rutile phase</td>
<td>89</td>
</tr>
<tr>
<td>TiCl$_3$ soln was introduced under vigorous stirring in deionized water. pH adjusted between 0.5 and 6.5 with NaOH. The solution heated at 60 °C for 24 h.</td>
<td>Anatase, rutile and brookite phases</td>
<td>90</td>
</tr>
<tr>
<td>Hydrothermal treatments of aqueous TiCl$_3$ solution containing large amt of NaCl through formation of oxo species</td>
<td>Rutile</td>
<td>91</td>
</tr>
<tr>
<td>By reacting a mixed solution of TiCl$_3$ and urea at 70°C for ~ 2h</td>
<td>Brookite</td>
<td>92</td>
</tr>
<tr>
<td>Reacting TiCl$_3$ in HCl with benzoyl peroxide taken in benzene &amp; autoclaved at 60 °C</td>
<td>1D nanorods of rutile</td>
<td>93</td>
</tr>
<tr>
<td>Forced hydrolysis of TiCl$_3$ in boiling 5M HCl solutions</td>
<td>Nanosize agglomerates</td>
<td>94</td>
</tr>
<tr>
<td>Method involving homogeneous precipitation in hexamethylenetetramine-TiCl$_3$-alcohol aqueous solutions</td>
<td>N doped TiO$_2$ anatase, rutile, brookite</td>
<td>95</td>
</tr>
<tr>
<td>TiCl$_3$ was mixed with Na$_2$S solution and pH was adjusted by addition of NH$_3$, followed by filtration and calcination</td>
<td>N doped TiO$_2$</td>
<td>96</td>
</tr>
</tbody>
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### Table 1.4: A brief literature status of TiO\textsubscript{2} synthesis using titanium tetrachloride as precursor

<table>
<thead>
<tr>
<th>Method of synthesis</th>
<th>General</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flame oxidation of TiCl\textsubscript{4}</td>
<td>Rutile</td>
<td>97</td>
</tr>
<tr>
<td>Hydrolysis of TiCl\textsubscript{4} at 70 °C for several hours</td>
<td>Rutile</td>
<td>98</td>
</tr>
<tr>
<td>Using nano rutile as seed to enhance the hydrolysis rate of TiCl\textsubscript{4}</td>
<td>Rutile</td>
<td>99</td>
</tr>
<tr>
<td>Simple aqueous phase stirring of TiCl\textsubscript{4} and HCl at low temperature</td>
<td>Flower like rutile titania nanocrystals obtained</td>
<td>100</td>
</tr>
<tr>
<td>Thermohydrolysis of TiCl\textsubscript{4} at 100 °C in various aqueous solutions</td>
<td>Mixtures of anatase, rutile and brookite were obtained</td>
<td>101</td>
</tr>
<tr>
<td>Heating aqueous TiCl\textsubscript{4} solution with not more then 1M Ti\textsuperscript{4+} at 80-150 °C</td>
<td>Brookite and rutile TiO\textsubscript{2}</td>
<td>102</td>
</tr>
<tr>
<td>Non hydrolytic sol gel reaction of TiCl\textsubscript{4} and benzyl alcohol</td>
<td>Nanocrystalline anatase TiO\textsubscript{2} obtained</td>
<td>103</td>
</tr>
<tr>
<td>Hydrolysis of TiCl\textsubscript{4} in NH\textsubscript{4}OH followed by addition of thiourea</td>
<td>N-S co-doped TiO\textsubscript{2}</td>
<td>104</td>
</tr>
</tbody>
</table>
In recent years, an exponential growth has been seen in the synthesis of TiO$_2$ nanomaterials owing to its applications ranging from photocatalysis and photovoltaic to sensors. TiO$_2$ at nanometer scale shows new physical and chemical properties that have been promising in many applications due to high photocatalytic activity [105,106], excellent gas sensitive properties [107] and dielectric properties [108]. Depending upon the choice of precursor, a variety of nanostructured TiO$_2$ materials with different morphologies including nanowires [109,110], nanotubes [111-113], nanorods [114], nanowhiskers [115] have been successfully synthesized. Various methods involved in synthesis of TiO$_2$ nanomaterials have been reviewed by Chen et al [107]. However, though significant advances have been made in the synthesis of TiO$_2$ nanoparticles, problems such as agglomeration of ultrafine nanocrystals into larger particles, difficulty in the recovery of TiO$_2$ nanocrystals [116] and health risks owing to the nanosize [117] TiO$_2$ still remain unsolved.

On the other hand, mesoporous TiO$_2$ with high surface area, large pore volume and pore diameter has triggered extensive research because of the potential application in the field of catalysis [118-120], separation technology [121,122], polymerization [123], nanoelectronics [124] and photocatalytic activity [125]. Various methods such as sol-gel method [126-129], evaporation induced self assembly (EISA) [130], chemical vapor deposition [131], facile chemical process [132], supercritical CO$_2$ mimicking [133] etc. have been employed for the synthesis of mesoporous TiO$_2$. 
The conventional method of preparation of mesoporous nanostructures is based on a liquid crystal templating mechanism. However this method is fairly long and is a multiple-step process [134]. The research to produce one step synthesis of anatase or nanocrystalline TiO$_2$ powder at low temperature still continues.

We report in our work, synthesis of TiO$_2$ using TiCl$_3$ as it is a convenient precursor of TiO$_2$. The use of alkoxide was avoided as it warrants tight control of experimental conditions like pH, humidity etc. because of the intense hydrolysis of the alkoxide in air. The high cost of alkoxide also limits the commercialization of such process. TiCl$_4$ is difficult to handle as it fumes easily. It is also reported that the TiO$_2$ synthesized using titanium sulphate is comparatively less active [135].

We synthesized S-doped TiO$_2$ by use of TiCl$_3$ and thiourea [136]. The detail of the synthesis procedure is described in Chapter II.

Some of the precursors and synthetic strategies adopted in literature for the synthesis of S-doped TiO$_2$ are summarized in Table 1.5.
Table 1.5: Literature status for synthesis of S-doped TiO$_2$

<table>
<thead>
<tr>
<th>Method</th>
<th>Precursor for TiO$_2$ and Sulphur</th>
<th>Reaction Conditions</th>
<th>Phase</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealing</td>
<td>TiS$_2$</td>
<td>Oxidative annealing</td>
<td>Anatase</td>
<td>137</td>
</tr>
<tr>
<td>Chemical</td>
<td>Ti(OC$_3$H$_7$) thiourea</td>
<td>Mixed with ethanol concentrated under reduced pressure</td>
<td>Anatase</td>
<td>138</td>
</tr>
<tr>
<td>Hydrothermal</td>
<td>TiO$_2$ (Xerogel) CS$_2$/ethanol fluid</td>
<td>Treated under supercritical conditions at 280 °C</td>
<td>Anatase Rutile</td>
<td>139</td>
</tr>
<tr>
<td>Sol-gel</td>
<td>Ti(IV)diisopropoxide bis(2,4-pentadionate) thiourea</td>
<td>Mixed with isopropanol Calcined at 550 °C</td>
<td>Anatase Rutile</td>
<td>140</td>
</tr>
<tr>
<td>Hydrothermal</td>
<td>Ti(SO$_4$)$_2$ thiourea</td>
<td>Autoclaved at 130 °C for 20 h</td>
<td>Anatase</td>
<td>141</td>
</tr>
<tr>
<td>Hydrolysis</td>
<td>TiCl$_4$ thiourea</td>
<td>Vigorous stirring followed by aging and vacuum drying</td>
<td>Anatase</td>
<td>142</td>
</tr>
<tr>
<td>Hydrothermal</td>
<td>TiCl$_4$ thiourea</td>
<td>Autoclaved at 180 °C for 20 h</td>
<td>Anatase</td>
<td>143</td>
</tr>
<tr>
<td>Solvothermal</td>
<td>Ti(SO$_4$)$_2$ (NH$_4$)$_2$S</td>
<td>Autoclaved at 200 °C for 4 h</td>
<td>Anatase</td>
<td>144</td>
</tr>
<tr>
<td>Hydrothermal</td>
<td>TiS$_2$</td>
<td>Autoclaved at 180 °C for 12 h</td>
<td>Anatase</td>
<td>145</td>
</tr>
<tr>
<td>Annealing</td>
<td>Commercial TiO$_2$ thiourea</td>
<td>Annealing at 400 °C for 1 h</td>
<td>-</td>
<td>146</td>
</tr>
<tr>
<td>Mechano-chemical</td>
<td>TiCl$_4$ thiourea</td>
<td>Ball milling of as obtained Ti(OH)$_4$ and thiourea</td>
<td>Anatase Rutile</td>
<td>147</td>
</tr>
</tbody>
</table>
Another method adopted for synthesis was hydrolysis of TiCl$_3$ with the aim of rapid synthesis of TiO$_2$.

A detail of the synthetic strategy employed for TiO$_2$ synthesis by this method is described in Chapter II.

Synthesis of TiO$_2$ is a subject of hot pursuit and there is still a need to explore new methods of preparing TiO$_2$ materials in terms of simplicity, lower manufacturing cost and high performance.
1.5. Surface Characterization Techniques

In heterogeneous catalysis, the reaction occurs at the surface of the catalyst. Catalytic surfaces hence need to be characterized with reference to their physical properties. A brief discussion of each method of characterization technique is presented in the following section.

a) X-Ray Diffraction Analysis

X-Ray diffraction is the most crucial technique in structure determination of crystalline solids. In XRD, a beam of X-rays with a wavelength ranging from 0.5 to 2 Å, incident on a specimen is diffracted by the crystalline phases in a specimen according to Bragg’s law [148]

\[ n\lambda = 2d \sin \theta \]

where, \( n \) is the order of reflection, \( \lambda \) the wavelength of X-Rays, \( \theta \) Bragg angle and \( d \) the interplanar spacing.

The three main types of information in a diffraction pattern include the position, the intensity and the shape of diffraction peaks. Comprehensive libraries of available characteristic d- spacings and intensities (JCPDS-files) of previously studied solids are available for comparative purposes.

Figure 1.9 (A), (B) shows the wide angle X-ray diffraction patterns of anatase and rutile titania respectively [149]. The former was formed after calcinations of the precursor at 350 °C.
It was found that all the sharp features observed in XRD pattern Figure 1.9 (A), are consistent with anatase phase. When anatase titania was heated to 700 °C rutile titania was formed as indexed in Figure 1.9 (B).

**Figure 1.9:** XRD spectra of (A) anatase titania (B) rutile titania [149]

In addition to characterization of various crystalline forms, XRD can also be used to find out average particle size of the crystallites using Debye-Scherrer formula

\[ t = \frac{k\lambda}{\beta \cos \theta} \]

where, \(k\) is a coefficient (0.89)

\(\lambda\) is the wavelength characteristic of the Cu K\(\alpha\) radiation,

\(\beta\) is the full width at half maximum (in radians),

and \(\theta\) is the angle at which 100 intensity peak appears.
b) UV-Vis Spectroscopy

Ultraviolet-visible spectroscopy (UV-Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. UV-Vis absorption spectroscopy measures the percentage of radiation that is absorbed at each wavelength. Typically this is done by scanning the wavelength range and recording the absorbance. It is widely used in organic chemistry to investigate the extent of multiple bond or aromatic conjugation within molecules. The technique can be expanded to gases and solids, and also beyond absorption, to include measured reflected rather than transmitted light.

It is also used for the measurement of electronic band gap of semiconductor films. Figure 1.10 shows the UV-Vis absorption spectra of anatase and rutile titania nanofibers. The absorption wavelength for anatase TiO$_2$ was found to be 385 nm and the corresponding band gap energy was 3.2 eV, whereas the absorption wavelength for rutile TiO$_2$ was found to be 420 nm and the corresponding band gap energy was 3.0 eV.
Figure 1.10: UV-Vis absorption spectra of anatase (A) and rutile (R) titania [149]

Band gap energies were calculated using the relationship of photon energy and frequency (c/λ): \( E = \frac{hc}{\lambda} \)

where, \( h \) is Planck’s constant (6.626 x 10\(^{-34}\) Js)
\( c \) is the speed of light (2.998 x 10\(^8\) m/s)
and \( \lambda \) is the wavelength of light.

The band gap of the samples can also be determined by the equation

\( E_g = \frac{1239.8}{\lambda} \) [150]

where, \( E_g \) is the band gap (eV)

\( \lambda \) (nm) is the wavelength of the absorption edges in the spectrum.
c) Thermal Analysis (TG/DTA)

Thermogravimetry or Thermogravimetric Analysis (TGA) provides a quantitative measurement of any weight changes associated with thermally induced transitions. The rates of these thermally induced processes are often a function of the molecular structure. TGA provides information on the thermal stability of the material. In TGA the weight of a sample is being continuously recorded over a period of time under controlled heating rate.

In differential thermal analysis (DTA), the difference in temperature between the sample and a thermally inert reference material is measured as a function of temperature usually the sample temperature. Any transition that the sample undergoes results in liberation or absorption of energy by the sample with a corresponding deviation of its temperature from that of reference.

Figure 1.11 shows the total weight loss of the titania precursor in the temperature region 0-1000 °C investigated by TG analysis [151].
Figure 1.11: TG-DTA curves of the TiO$_2$ precursor solution [151]

There is no appreciable weight loss observed beyond 400 °C. The weight loss consists of two distinct steps at 250 °C and 350 °C which may result from the decomposition of the peroxy group. In DTA curve, two obvious thermal effects are detected: an endothermic peak at 100 °C and a broad exothermic peak centered at 780 °C. The former is accompanied by obvious weight loss steps which may be due to release of adsorbed water, while the exothermic peak that shows no weight change may be attributed to the phase transformation from anatase to rutile.
d) BET Surface Area and Pore volume Measurements

Surface areas were obtained by the physical adsorption of monolayer of nitrogen gas (area = 0.162 nm$^2$) at -196 °C from Brunauer-Emmett-Teller (BET) adsorption isotherm measurements. The surface area calculated from the use of BET equation is perhaps the most popular and widely used in the literature, ever since Brunauer, Emmett and Teller (BET) derived the equation for physical adsorption of gases on solid surfaces that lead to multilayer adsorption. The simple form of this equation that forms the basis of the BET method for the determination of surface area of solids can be written as

$$\frac{P}{V(P_o - P)} = \frac{1}{V_mC} + \frac{P(C-1)}{V_mP_oC} \quad [152]$$

where, $V$ is the volume of gas adsorbed at equilibrium pressure, $P$ and $P_0$ is the saturated vapour pressure of the adsorbate at liquid nitrogen temperature and $C$ is the isothermal constant.

The N$_2$ adsorption and desorption isotherm of the TiO$_2$ sample synthesized by using TiCl$_3$ precursor and NH$_3$ as precipitating agent is given in Figure 1.12 [153].
Figure 1.12: \( \text{N}_2 \) adsorption-desorption isotherm and pore size distribution of synthesized TiO\(_2\) sample [153]

Shape of the isotherm shows a typical type IV isotherm with a clear hysteresis at a relatively low pressure, which indicates a mesoporous nature of the sample. Pore size distribution also confirms the mesoporous nature of the sample with an average pore size of around 4 nm.
e) Fourier Transform Infrared (FTIR) Spectroscopy

Infrared spectroscopy has been extensively used for identifying the various functional groups on the catalyst itself, as well as for identifying the adsorbed species and reaction intermediates on the catalyst surface. It is one of the few techniques capable of exploring a catalyst both in its bulk and its surface, and under actual reaction conditions. It is widely used for characterizing the acid sites of the catalyst, which are responsible for their catalytic properties. A typical FTIR spectra of TiO$_2$ sample [153] synthesized by different precipitating agent is given in Figure 1.13.

![FTIR spectra of TiO$_2$ samples S1, S2 and S3](image)

**Figure 1.13**: FTIR spectra of TiO$_2$ samples S1, S2 and S3 [153]

The FTIR spectrum shows a broadband around 3400 cm$^{-1}$ which is attributed to the O-H stretching mode of the surface adsorbed water molecule. Another band of around 1600 cm$^{-1}$ is attributed to the O-H bending mode. The bands around 400-900 cm$^{-1}$ are due to the Ti-O bond stretching mode of titania.
f) Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) is a well established technique used to study the topography, texture and surface features of powders. The SEM produces a three dimensional view of specimen and this is very useful in examining the shape and structure of a specimen. In SEM analysis an electron gun emits a beam of electrons which then interacts with the surface leading to emission of electrons from the surface of the specimen during the scanning with the electron beam. The electron from the beam interacts with the sample resulting in deflection of secondary particles to a detector which subsequently converts the signal to voltage and amplifies it. Figure 1.14 shows the SEM images of S1 (a), S2 (b) and S3 (c) synthesized by using TiCl$_3$ as the Ti precursor and varying precipitating agents such as NH$_3$, NaCl and NH$_4$Cl respectively [153].

Figure 1.14: SEM images of synthesized TiO$_2$ samples (a) S1, (b) S2, (c) S3 [153]

SEM images show agglomerated particles having cube like morphology, spherical morphology and rod like morphology for S1, S2 and S3 respectively.
g) Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) is a useful technique in determining crystal morphology and particle size of materials. In TEM a beam of electrons is propagated through a solid sample in a vacuum. Electrons transmitted through the sample are then detected to produce three dimensional images which represent the relative extent of penetration of electrons in a specific sample. TEM can be coupled with energy dispersive X-ray (EDX) analysis to obtain information about the chemical nature and composition of the sample. High Resolution TEM (HRTEM) allows for the determination of lattice spacings and direction of particles. The high resolution TEM images of the TiO$_2$ nanoparticles synthesized under various conditions [153] are shown in Figure 1.15.
Figure 1.15: HRTEM images of S1 (a) nanocubes and (b) corresponding lattice; S2 (c) nanospheres and (d) corresponding lattice [153]

TEM image of S1 (a) shows the formation of nanocubes with particle size around 25 nm. The HRTEM image (b) shows lattice fringes of the anatase phase. The fringes with $d = 0.34$ nm match with that of the (101) crystallographic plane of anatase titania, which confirms that S1 is a single crystalline anatase phase. Sample S2 (c) shows the formation of nanospheres of average crystallite size around 8 nm. The lattice image (d) of these nanospheres shows lattice fringes of the rutile phase with $d = 0.32$ nm, which matches well with that of (110) plane of rutile titania.
h) Surface Acidity Measurements

Temperature Programmed Desorption technique is one of the most widely used and flexible techniques for characterizing the acidic/basic sites on oxide surface. The acidity or basicity of the catalyst is measured by desorbing probe molecules like ammonia or CO$_2$ respectively, adsorbed on solid surface by heating it at a programmed rate. Figure 1.16 (a) and (b) [154] gives the TPD spectra for desorption of CO$_2$ and NH$_3$, respectively on A2 (pure anatase) and R2 (pure rutile).

![Figure 1.16 (a): TPD CO$_2$ spectra of TiO$_2$ A2- pure anatase; R2-pure rutile][154]

![Figure 1.16 (b): TPD NH$_3$ spectra of TiO$_2$ A2-pure anatase; R2-pure rutile][154]

It is clear from Figure 1.16 (a), that both these catalysts have similar distribution of basic sites. Both show a predominant peak due to weak basic sites. On the other hand as seen from figure 1.16 (b), R2 (rutile) has large acidity which is due to weak Lewis acid sites whereas acidity incase of A2 (anatase) is due to presence of strong Lewis acid sites.
i) X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the material being analyzed. Electrons are counted and then separated according to their energy. The energy of photoelectrons is related to atomic and molecular environment. Number of electrons emitted is proportional to the concentration of the emitting atom on the surface. XPS requires ultra high vacuum (UHV) conditions.

High resolution XPS data of the Ti 2p region comparing rutile and anatase titania is shown in Figure 1.17 [149].
As seen in Figure 1.17, the doublet peaks of Ti 2p were observed at 459 (Ti 2p$_{3/2}$) and 465 (Ti 2p$_{1/2}$) eV in both rutile and anatase titania. These are the characteristic Ti 2p XPS features of titania. The similar peak positions for both forms of titania imply that the core level binding energy of Ti on the surface does not depend significantly on the crystal structure.

**Figure 1.17** High resolution XPS spectra of the Ti 2p region (A = anatase; R = rutile) [149]
j) **Raman Spectroscopy**

Raman spectroscopy can be thought of as a means to measure the inelastic light scattering which results from the excitation of the vibrations in molecular and crystalline materials all as a function of wavenumber. The monochromatic light used in Raman scattering is usually from a laser in the visible, near infrared or near ultraviolet region. Excitations in the system are absorbed or emitted by the laser light, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the photon modes in the system. The Raman spectra of the synthesized anatase TiO$_2$ and Degussa [155] are shown in Figure 1.18.
Figure 1.18: Raman spectra of (a) Degussa TiO$_2$ and (b) anatase TiO$_2$ [155]

The vibration mode symmetries of the anatase are indicated in Figure 1.18. Raman peaks at 156.9, 206, 408.48, 529.54, 649.4 and 801 cm$^{-1}$ were assigned to $E_g$, $E_g$, $B_{1g}$, $A_{1g}$, $E_g$ and $B_{1g}$ respectively. The peak positions and intensities of the six Raman active modes correspond well with the anatase phase of TiO$_2$. No significant broadening or shift of Raman spectra was observed in synthesized anatase TiO$_2$ in comparison to bulk Degussa TiO$_2$. 
n) Point of Zero Charge (pzc)

Solid metal oxides in contact with aqueous solutions typically become hydrated and form a monolayer of surface hydroxyl groups that may become protonated or deprotonated, depending on the $H^+$ (aq) concentration. This amphoteric behaviour allows the oxide particles to develop electrical charges that are either positive, when they receive protons (equation 1) or negative, when they release protons (equation 2).

\[
\text{M-OH(surf)} + H^+ (\text{aq}) = \text{M-OH}_2^+ (\text{surf}) \quad \text{-----pK}_1 \quad (1)
\]

\[
\text{M-OH(surf)} + \text{OH}^- (\text{aq}) = \text{M-O}^- (\text{surf}) + \text{H}_2\text{O(l)} \quad \text{-----pK}_2 \quad (2)
\]

The resulting net charge $Q$, may be defined as the difference in concentration between the positive and negative sites per weight of the solid.

\[
Q = \{\text{M-OH}_2^+ (\text{surf})\} - \{\text{M-O}^- (\text{surf})\} \quad \text{----- (3)}
\]

If the concentrations of the two types of sites resulting in equation 1 and 2 are the same, there will be no net charge on the surface. This condition is called the point of zero proton charge, pzpc (or zero proton condition, zpc).

The pzpc can thus be measured by potentiometric titration if $H^+$ and $\text{OH}^-$ are the only aqueous ions involved. In practice, however, electrolytes typically contain other anions, $A^-$ and cations, $C^+$ that may adsorb onto the surface sites as follows:

\[
\text{M-OH}_2^+ (\text{surf}) + A^- (\text{aq}) = \text{M-OH}_2 + A^-(\text{surf}) \quad \text{----- (4)}
\]

\[
\text{M-OH}_2^+ (\text{surf}) + C^+ (\text{aq}) = \text{M-O}^- C^+(\text{surf}) + 2H^+ (\text{aq}) \quad \text{----- (5)}
\]

In these cases the net surface charge not only depends on the $H^+$ and $\text{OH}^-$ ions in the medium, but also on the concentration of the electrolyte [that provides $A^-(\text{aq}), C^+(\text{aq})$].
The pH of the aqueous solution at which the sum of the all the surface positive charges balances the sum of all the surface negative charges is called the *point of zero charge*, \( pzc \).

A simple and fast method that gives a reasonable approximation to the \( pzc \) consists in locating the intersection of one or more titration curves performed with constant ionic strength and different amounts of solid, and that of a blank solution (i.e., without the solid). This is called the *potentiometric mass titration method, PMT* [156]. This method is better understood by analyzing the plot in Figure 1.19 with the aid of the explanation given below.

**Figure 1.19**: Determination of point of zero charge by potentiometric mass titration technique [156]
The points $a$, $b$ and $c$ in Figure 1.19 correspond to the blank solution, and $d$, $e$, $f$ and $g$ correspond to the sample. The blank solution consists of $w$ mL of a solution of an inert, supporting electrolyte (e.g., KNO$_3$) of concentration $x$; thus, the point at $a$ corresponds to the natural pH of this solution. Upon addition of $y$ mL of NaOH of concentration $z$, the pH of the blank increases to $b$. By doing potentiometric titration with a strong acid (e.g., HNO$_3$), the blank curve is generated ($c$ is an arbitrary final point).

The initial pH of the sample solution (composed of $w$ mL of the inert electrolyte solution plus $m$ grams of the solid oxide, MOH) is at $d$ (i.e., below the pzc) due to the removal of H$^+$ from the solution by the neutral surface sites in M-OH to form M-OH$_2^+$ (eq. 1). Then, addition of the same $y$ mL of $z$ M NaOH to this suspension of the sample brings it to the point $e$, which is below $b$. This is because the OH$^-$ added play three roles: it serves to neutralize the H$^-$ (aq) and the MOH$_2^+$ (surf) created during the $a \rightarrow d$ step, removes H$^+$ (surf) from the resulting MOH sites so as to create basic sites (MO$^-$) at the oxide surface.

By doing a potentiometric titration, the H$^-$ (aq) added from $e$ to $f$ (see Region I of the sample curve) play two roles: some of them neutralize the OH$^-$ (aq), and the others neutralize the MO$^-$ (surf). This is the reason for the smaller pH values in this curve as compared to those in the blank curve. On the other hand, the H$^+$ (aq) added from $f$ to $g$ (Region II of the sample curve) also play two roles: a minor role, i.e., to neutralize the (small amount of) OH$^-$ (aq) remaining in solution and a major role, i.e., to protonate the neutral M-OH(surf) sites.
The difference in pH between the sample and blank curves in this region will therefore be almost proportional to the amount of solid sample in the suspension.

Between the end of Region I and the beginning of Region II in the sample curve, there is a small region (or even a single point, \( f \)) where all the \( H^+ \) added serve to neutralize the \( OH^- \), just as they do in the blank curve. For this reason both curves intersect at this point, which is then identified as the pzc. This intersection should appear at the same pH value for any amount of oxide placed in the solution [156].
1) Photoluminescence

Photoluminescence (PL) spectroscopy is a non-destructive method of probing the electronic structure of materials. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo-excitation. One way this excess energy can be dissipated by the sample is through the emission of light, or luminescence. In the case of photo-excitation, this luminescence is called photoluminescence. The intensity and spectral content of this photoluminescence is a direct measure of various important material properties. Photo-excitation causes electrons within the material to move into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released and may include the emission of light (a radiative process) or may not (a nonradiative process). The energy of the emitted light (photoluminescence) relates to the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state. The quantity of the emitted light is related to the relative contribution of the radiative process. Various excitation wavelengths allow for varying penetration depths into the material, and thus, varying levels of volume excitation.

Figure 1.20 shows the PL spectra of various TiO$_2$ samples synthesized by solvothermal method [157].
The excitation wavelength employed was 260 nm. All spectra showed similar broad peaks in the wavelength region from 370 to 500 nm. A broad asymmetric peak centered around 410 nm has been attributed to the defects present on the surface of TiO$_2$ nanoparticles. The peaks marked with "*" in the spectra correspond to artifacts and was confirmed by recording the emission spectrum of the samples by slightly changing the excitation wavelength. It was observed that the genuine peaks do not get shifted, whereas the artifacts get shifted with change in excitation wavelength.
1.6. Titania as a catalyst and catalyst support

Titania as a catalyst exhibits a number of attractive characteristics such as chemical stability, non-toxicity, low cost and the highest oxidation rate as compared to many active metal oxides investigated. Titania presents increasing interest as a catalyst or catalyst support. However depending upon synthesis methods there could be some disadvantages associated with titania which could be low surface area, poor thermal stability, poor mechanical strength and lack of abrasion resistance [158-161].

This has been partially overcome by the application of new synthesis procedures in order to obtain titania with high surface area [162-164]. It is important to control the phase, particle size, the presence of defects and morphology of TiO₂ during the synthesis. The use of nanosized TiO₂ which is accompanied by the surface area enhancement as well enhanced optical properties of the material holds promise in catalysis both as active phase and support. For many applications, supported oxides are more efficient and therefore titania supported catalysts are also interesting as an active catalyst component or as support [165,166]. The support in addition to being a carrier often interacts with the active components to form surface compounds that may or may not be catalytically more active. The porous nature of the support often allows higher dispersion of the active component, which results in the use of small amount of the active component. It also affects the overall conversion and selectivity of the catalyst. The desire to produce well structured, porous, high surface area and complex forms of titania based materials has also led to the development of titania nanotubes [167].
The surface properties of the catalysts that facilitate adsorption process favourably influence the catalytic activity. Some of these properties are surface area, particle size, colloidal size, pzc. Of primary importance are the surface hydroxyls or Bronsted acid sites. The organic reactions catalyzed by TiO\textsubscript{2}, like in any other oxides are due to its acid-base properties in these systems. There may be both Bronsted acidity as well as simultaneous presence of Lewis acid-base pairs on TiO\textsubscript{2}. Some of the reactions studied on the TiO\textsubscript{2} include reduction of aldehydes to give ketones [168,169], cyclization of alkynes [170-172], dehydration of alcohols to give olefins [168,172], dehydration of carboxylic acid [173,174], dehydrogenation of alcohols [172,175], condensation of aldehydes [169,176] and coupling of carboxylic acid to form ketones [173,174].

TiO\textsubscript{2} is also active catalyst used in hydrocarbon selective oxidation processes [177] and dimerisation of formaldehyde to methyl formate [178]. TiO\textsubscript{2} finds application as a support for metal catalysts which are active in CO hydrogenation [179] and oxidation with NO [180] and O\textsubscript{2} [181]. Strong metal support interaction (SMSI) was first reported for noble metals supported on TiO\textsubscript{2} [182,183]. Numerous other reactions such as oxidation of H\textsubscript{2}S to SO\textsubscript{2}, isomerization and alkylation reactions have been studied by employing TiO\textsubscript{2} catalysts.
1.7. TiO$_2$ as a photocatalyst

![Diagram of photocatalysis]

**Figure 1.21:** TiO$_2$ as a photocatalyst [184]

In 1972, Fujishima and Honda [2-4] discovered the photocatalytic splitting of water on TiO$_2$ electrodes and the event marked the beginning of a new era in heterogeneous photocatalysis. Photocatalysis is basically a reaction which uses light to activate a catalyst (photocatalyst) and thus alter the speed of a chemical reaction by lowering the activation energy for the primary reaction to occur.

Some of the properties of TiO$_2$ such as chemical and biological inertness, strong oxidizing power, long term stability against corrosion, water stability and non toxicity makes it environmentally harmonious photocatalyst.
In recent years, when there is increasing awareness for protection of environment from hazardous wastes and effluents. TiO$_2$ has shown a great potential for detoxification of both air and water in heterogeneous photocatalytic processes as well as for degradation of VOCs [185]. The photocatalytic properties arise mainly due to favourable band gap of this semiconductor in addition to several other properties. Photocatalytic reactions at the surface of titanium dioxide have been attracting much attention for practical applications such as self cleaning of tiles, glasses and windows. It can also be used as antibacterial agent because of strong oxidation activity and superhydrophilicity [186]. The surface of TiO$_2$ has a very high oxidation potential which makes it capable of breaking down many organic substances. A semiconductor under UV light generates holes and electrons. The photocatalyst is active if the holes and electrons have a sufficiently long life so as to allow them to migrate to the particle surface and get trapped by the surface active sites. However many photocatalysts are inactive due to faster electron-hole recombination than the charge transfer process. The photocatalytic mechanism is initiated by the absorption of the photon $h\gamma$ with energy equal to or greater than the band gap of TiO$_2$ ($\sim 3.3$ eV for anatase phase) producing an electron-hole pair on the surface of TiO$_2$ as shown in figure 1.22. An electron is promoted to the conduction band (CB) while a positive hole is formed in the valence band (VB).
Excited state electrons and holes can recombine and dissipate the input energy as heat, get trapped in metastable surface states, or react with electron donors and electron acceptors adsorbed on the semiconductor surface or within the surrounding electrical double layer of the charged particles. After reaction with water, these holes can produce hydroxyl radicals with high redox oxidizing potential. Depending upon the exact conditions, the holes, OH radicals, O$_2^-$, H$_2$O$_2$ and O$_2$ can play important roles in the photocatalytic reaction mechanism [188].
The usual mechanistic steps of TiO$_2$/UV process are shown in scheme 1.1.

\[
\begin{align*}
\text{TiO}_2 + h\nu & \rightarrow \text{TiO}_2 (e^-, h^+) \\
\text{TiO}_2 (h^+) + RX & \rightarrow \text{TiO}_2 (RX^+) \text{ ads} \\
\text{TiO}_2 (h^+) + \text{H}_2\text{O}/\text{OH}^- & \rightarrow \text{TiO}_2 (\text{OH}) \text{ ads} + H^+ \\
\text{TiO}_2 (e^-) + O_2 & \rightarrow \text{TiO}_2 (\text{O}_2^-) \text{ ads} \\
\text{TiO}_2 (\text{RX}^+) \text{ ads} + \text{TiO}_2 (\text{OH}) \text{ ads} & \rightarrow \text{TiO}_2 (\text{R-OH}) \text{ ads} + X^- \\
\text{TiO}_2 (\text{R-OH}) \text{ ads} + \text{OH} & \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]

**Scheme 1.1:** Mechanism for the TiO$_2$/UV process

Photocatalytic reduction of organic and metal containing ions, oxidation of volatile organic or inorganic compounds in the gas phase including NOx and SOx, studies on cell killing and disinfection by illuminated titanium dioxide have also received increasing attention in recent years [189,190]. Consequently in Japan, United States and China commercialization of TiO$_2$ has been initiated in various fields such as exterior construction materials, interior furnishing materials, road construction materials, purification facilities and household goods.

Despite the positive attributes of TiO$_2$ as an ideal photocatalyst, there are some drawbacks associated with its use in charge carrier recombination, poor adsorption properties, difficulty in separation etc. Hence to obtain a good photocatalyst, proper control of the structural parameters such as particle size, crystalline quality, morphology, surface area is of crucial importance during the catalyst synthesis.
1.8. Reactions selected for the present study

For the present investigation catalytic reactions like a) epoxidation of olefins and b) benzylation of aromatics were carried out on synthesized titania systems. The photocatalytic degradation of dyes like Methylene Blue and Congo Red was also carried out successfully.

a) Epoxidation reactions are indispensable for the chemical industry because the epoxides are valuable and versatile commercial intermediates, used as key raw materials for a wide variety of products owing to the numerous reactions they may undergo. We studied the epoxidation of cyclohexene and cis-cyclooctene. Epoxidation reactions of alkenes generally require the presence of a catalyst. TiO$_2$ as such is inactive for the epoxidation. However Ti or TiO$_2$ bonded to siloxanes are considered to be active. The types of catalysts investigated for epoxidation reactions and the observed reactivity/selectivity have been summarized in Table 1.6.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction and Reaction Conditions</th>
<th>%C</th>
<th>%S</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$-SiO$_2$ gels</td>
<td>Ciscyclooctene, methanol, H$_2$O$_2$, catalyst, temp 70 °C, 4 h</td>
<td>~35</td>
<td>&gt;95</td>
<td>191</td>
</tr>
<tr>
<td>TiO$_2$-SiO$_2$ mixed oxides</td>
<td>Cyclohexene, TBHP, Catalyst, temp. 70 °C</td>
<td>~95</td>
<td>~95</td>
<td>192</td>
</tr>
<tr>
<td>Ti in MCM-41 framework</td>
<td>Cyclohexene, H$_2$O$_2$, catalyst, temp. 70 °C</td>
<td>05</td>
<td>-</td>
<td>193</td>
</tr>
<tr>
<td>Ti on surface of MCM-41</td>
<td>Cyclohexene, H$_2$O$_2$, catalyst, temp. 70 °C</td>
<td>50</td>
<td>100</td>
<td>193</td>
</tr>
<tr>
<td>ZrO$_2$-TiO$_2$</td>
<td>Cyclooctene, TBHP, n-decane, catalyst, temp. 70 °C</td>
<td>11</td>
<td>100</td>
<td>194</td>
</tr>
<tr>
<td>SiO$_2$-TiO$_2$</td>
<td></td>
<td>25</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$-TiO$_2$</td>
<td></td>
<td>28</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>Ti-SBA(65)-573</td>
<td>Cyclooctene, acetonitrile, H$_2$O$_2$, catalyst, temp. 70 °C</td>
<td>50</td>
<td>100</td>
<td>195</td>
</tr>
<tr>
<td>Ti-SBA(65)-573</td>
<td>Cyclohexene, acetonitrile, H$_2$O$_2$, catalyst, temp. 70 °C</td>
<td>07</td>
<td>100</td>
<td>195</td>
</tr>
<tr>
<td>RuO$_2$ loaded mesoporous TiO$_2$</td>
<td>Cyclohexene, tert butanol, H$_2$O$_2$, catalyst, temp. 70 °C</td>
<td>14</td>
<td>06</td>
<td>196</td>
</tr>
<tr>
<td>RuO$_2$ loaded mesoporous TiO$_2$</td>
<td>Cyclohexene, tert butanol, H$_2$O$_2$, catalyst, temp. 70 °C</td>
<td>35</td>
<td>80</td>
<td>196</td>
</tr>
<tr>
<td>Ti-MCM-41(25)</td>
<td>Cyclohexene, dry TBHP in DCM, CHCl$_3$, catalyst, temp. 60 °C, 6h</td>
<td>47</td>
<td>98</td>
<td>197</td>
</tr>
<tr>
<td>TiO$_2$-SiO$_2$ mixed oxide</td>
<td>Cyclohexene, acetonitrile, H$_2$O$_2$, catalyst, Temp. 70 °C</td>
<td>43</td>
<td>18</td>
<td>198</td>
</tr>
<tr>
<td>Titanium silicate Ti-MMM-2</td>
<td>Cyclooctene, acetonitrile, H$_2$O$_2$, catalyst, temp. 60 °C</td>
<td>-</td>
<td>-</td>
<td>199</td>
</tr>
</tbody>
</table>

**Conclusion:** No reports were available on TiO$_2$ alone being an active material for epoxidation reactions.
b) Benzoylation reaction constitutes an important class among acylation reactions due to the commercial importance of benzophenones in agrochemical industries. In the present investigation benzoylation of different substrates like toluene, anisole and o-xylene was carried out in presence of acylating agent and ZnO-TiO$_2$ composite catalyst. ZnO-TiO$_2$ composite catalysts have been studied for this reaction for the first time. A brief literature review on different catalysts used so far for the benzoylation reaction is summarized in Table 1.7.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction and Reaction Conditions</th>
<th>% C</th>
<th>% S</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₄/ZrO₂</td>
<td>Toluene, benzoyl chloride, catalyst, temp. 100 °C, 3h</td>
<td>60</td>
<td>68</td>
<td>200</td>
</tr>
<tr>
<td>SO₄/TiO₂</td>
<td>Toluene, benzoyl chloride, catalyst, temp. 100 °C, 3h</td>
<td>17</td>
<td>73</td>
<td>200</td>
</tr>
<tr>
<td>Fe promoted SO₄/ZrO₂</td>
<td>Toluene, benzoyl chloride, catalyst, temp. 110 °C</td>
<td>79.61</td>
<td>84</td>
<td>201</td>
</tr>
<tr>
<td>Fe promoted SO₄/ZrO₂</td>
<td>Xylene, benzoyl chloride, catalyst, temp. 110 °C</td>
<td>96.23</td>
<td>89</td>
<td>201</td>
</tr>
<tr>
<td>Borate Ziconia</td>
<td>Anisole, nitrobenzene, benzoyl chloride, catalyst</td>
<td>91</td>
<td>93.6</td>
<td>202</td>
</tr>
<tr>
<td>Zr-TMS</td>
<td>Toluene, p-toluoyl chloride, nitrobenzene, temp. 130 °C, 24h</td>
<td>85</td>
<td>73.9</td>
<td>203</td>
</tr>
<tr>
<td>Beta Zeolite</td>
<td>Anisole, acetic anhydride, catalyst, 120 °C</td>
<td>87</td>
<td>97</td>
<td>204</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>Anisole, acetic anhydride, catalyst, temp. 100 °C, 2h</td>
<td>90</td>
<td>-</td>
<td>205</td>
</tr>
<tr>
<td>STA-mesoporous alumina</td>
<td>Anisole, p-toluoyl chloride, catalyst, 120 °C</td>
<td>62.95</td>
<td>94.92</td>
<td>206</td>
</tr>
<tr>
<td>SO₄²⁻/SnO₂</td>
<td>Toluene, acetic anhydride, catalyst, 70 °C</td>
<td>-</td>
<td>95</td>
<td>207</td>
</tr>
</tbody>
</table>

**Conclusion:** No reports were available on ZnO-TiO₂ catalysts. Most of the catalysts used were acid functionalized and required a complex synthesis pathway.
1.9 Objectives of the present work

- To prepare nanocrystalline titania using TiCl$_3$ as a convenient precursor

- To prepare TiO$_2$ and its composites with ZnO

- To investigate the prepared titania for photocatalytic degradation of dyes

- To study the catalytic activity of prepared titania and its composites with ZnO, towards the liquid phase epoxidation and benzylation reactions
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